Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes

2014 DOE Vehicle Technologies Program Annual Merit Review

Project ID#: ES128

Principal Investigator: Sergey D. Lopatin

Project Manager: Ajey M. Joshi

Corporate CTO Office

Energy Storage Solutions

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Overview

Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes

PROJECT TIMELINE

Start: **10/01/2011** | End: **09/30/2014** | **~69%** Complete

BUDGET

Total Project Funding:	**$4.90M (51%)** DOE Share **$4.63M (49%)** Applied Materials
FY13 Funding Received:	**$1.60M**
FY14 Funding Expected:	**$1.70M** DOE Share

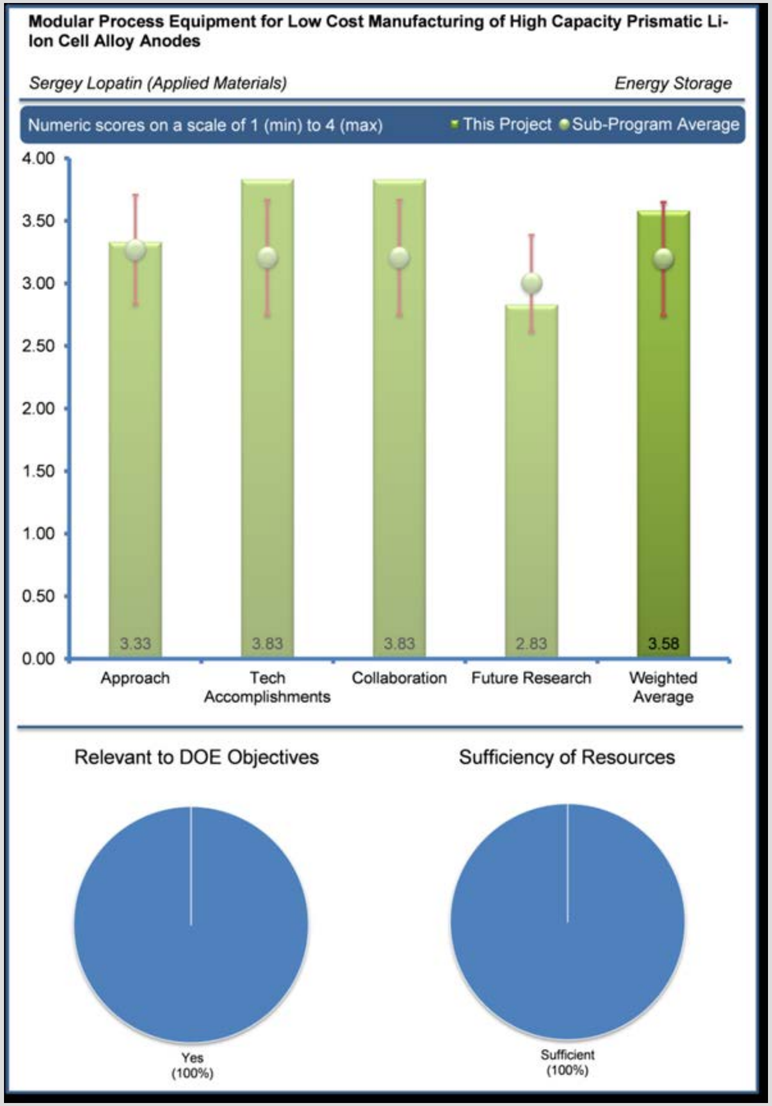
BARRIERS ADDRESSED

- **Cost of manufacturing**
- **Cycling lifetime of high capacity materials**
- **Prismatic cell format**

PARTNERS

- ***J. Nanda***, Oak Ridge National Laboratory
- ***G. Liu***, Lawrence Berkeley National Laboratory
- ***M. Yakovleva***, FMC Lithium
- ***P. Hagans,*** Navitas (former A123 Systems division)
- ***K. Oshihara***, Nissan-TCNA

Response to Reviewers Comments



- Relevance

Comments: The reviewers stated that this project has very strong relevance for the DOE goals of reducing the use of petroleum products to power vehicles. They noted that this unique manufacturing approach delivers a unique anode, which could facilitate appreciably higher performing EV cells.

Response: Navitas Systems is evaluating the Applied Materials electrodes using testing equipment for half coin cell, full coin cell, and full scale 63450 prismatic cell geometries. Finally, the Nissan Technical Center (North America) has a researcher who is conducting cell performance measurements and final cell validation to USABC requirements.

- Approach

Comments: One reviewer indicated that the equipment manufactured by Applied Materials will reduce the manufacturing cost of anodes. The reviewer stated that the coating width to meet the cost goals is needed for the success of the coating equipment.

Response: Cost remains a question at this point, it will be part of the final deliverable for reducing the manufacturing cost of anodes. This technology is expected to be scalable.

- Technical Accomplishments

Comments: The mechanical stability of this material may be a critical issue and should be addressed. The reviewer concluded that the key technical risks have to do with improving the process for forming the electrodes.

Response: Stanford Linear Accelerator Center granted beam-time for better understanding and controlling the stability of this material.

Objectives & Scope

Relevance

A. PROJECT OBJECTIVES

The objective of this project is to research, develop, and demonstrate novel high capacity Li-ion battery cell anodes that are capable of achieving an energy density of at least 500 Watthours per liter (Wh/l) and a power density of at least 500 Watts per liter (W/l) while maintaining comparable performance standards in terms of cycle life (300-1000 cycles at 80% depth of discharge), calendar life (5-10 years), and durable cell construction and design capable of being affordably mass produced.

B. PROJECT SCOPE

The project includes research, development, test, and demonstration of an advanced High Volume Manufacturing (HVM) prototype module for fabricating high capacity Li-ion anodes in a continuous roll-to-roll configuration at low cost. The HVM prototype module will manufacture a new class of Li battery anodes with a high capacity based on an innovative micro-cell porous 3D Cu – Li alloy structure. The project will focus on demonstrating the innovative high rate deposition technique suitable for the micro-cell porous 3D Cu – Li alloy architecture.

Technical Summary

BASELINE CHARACTERIZATION

A cell level design model has been developed for two chemistry combinations:

- Baseline cell having $Li_{1-x}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC333) positive electrode with 3D Cu Graphite negative electrode, and
- Interim cell having NMC positive electrode with 3D CuSn negative electrode.

TECHNOLOGY DESIGN

Experimental development focused on concept design of initial electro-deposition module which allows for 3D porous structure formation in a single prototype tool for both 3D Cu collector and 3D CuSnFe alloy anode coating.

- Baseline processes have been developed for (a) 3D Cu current collector and (b) for graphite coating using a water soluble process.
- Scanning Electron Microscopy (SEM) analysis of 3D Cu graphite structures shows pore fill and crack-free coating. Preliminary testing rate performance in half-cell assembly *vs.* Li demonstrated capacity retention advantages at 2C and 3C.

TECHNOLOGY DEVELOPMENT

For the high capacity, we have developed CuSnFe electro-deposition process and obtained nano-structure alloy for high loading NMC / CuSnFe cell testing.

Technical Summary

TECHNOLOGY DEVELOPMENT

- Eighteen cells comprised the program's 1st deliverable were sent to Idaho National Laboratory (INL) for further evaluation.
- Development of electro-deposition module which allows for 3D-porous structure formation in a single prototype tool for both 3DCu collector and 3DCuSnFe alloy anode.
- Development of modular technological steps for forming 2.5-4.5 mAh/cm^2 cells including process methodology for Graphite coating by water soluble process to achieve adhesion to the 3D-porous structures. Testing rate performance in half-cell assembly vs. Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates.
- Testing baseline pouch cell assembly. Porous 3D electrodes were assembled in single layer pouch cells with Li1-x[Ni1/3Mn1/3Co1/3]O2 (NMC) cathodes.The retention capacity for 3DCu/Graphite vs. NMC was measured 81.8% at 1310 cycles. Projection from these data is that the baseline cell is capable of over 1400 cycles at capacity retention of 80% at C/3 rate.
- Development of 3DCuSnFe nano-structure alloy anode. Coulombic efficiency (CE) is improved by grain size reduction, pre-lithiation, and mitigation with combining alloy with Graphite.
- Extending 3D electrode concept to the high loading 3DCuSnFe/Graphite alloy electrodes and testing interim pouch cell. The retention capacity of 76.2% at 1280 cycles was demonstrated. These data show that the interim cell is capable of 985 cycles at 80% capacity retention at C/3 rate.

Prototype Equipment
Electro-Deposition

Process Control
Ammeter
Voltmeter
Temperature
Conductivity

Sample Control
Uniformity
Roughness
Pore Size
Thickness
Weight

Cu Foil
3D Cu

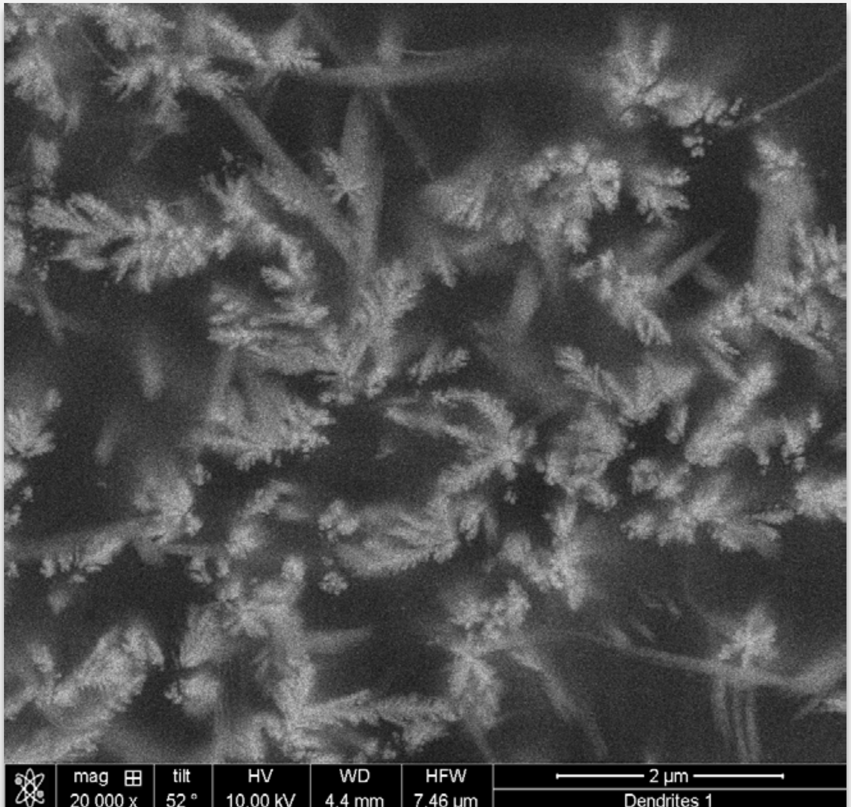
Plating Chamber1 3D Cu

Plating Chamber2 3D CuSnFe

Rinse Chamber3

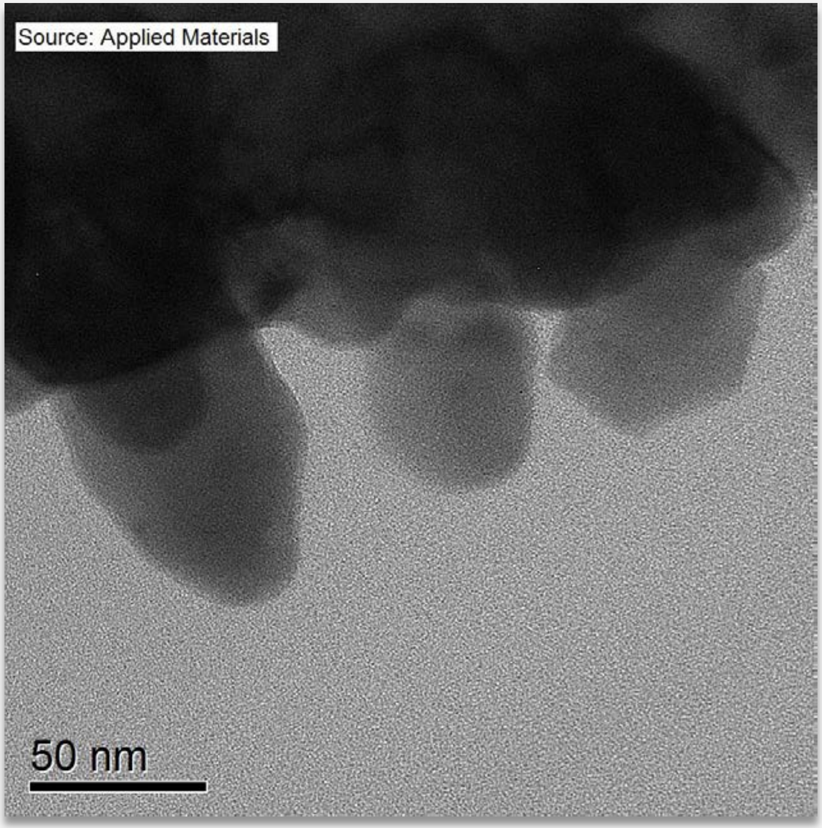
3D porous copper electroplating tool.

3D CuSnFe
High Resolution Images



SEM

Connected nano-grains form network of porous active material on Cu foil

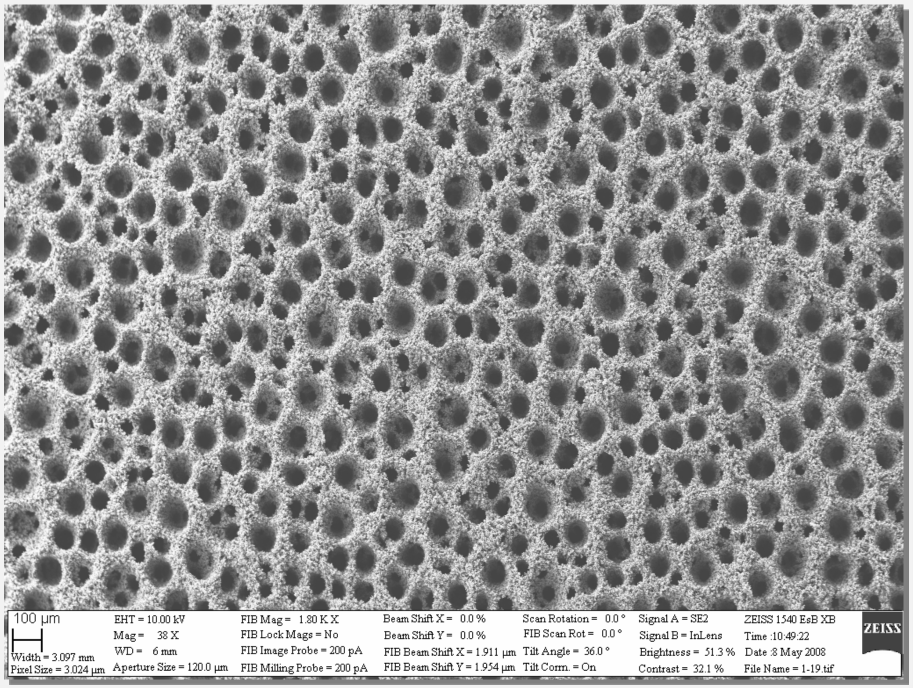


TEM

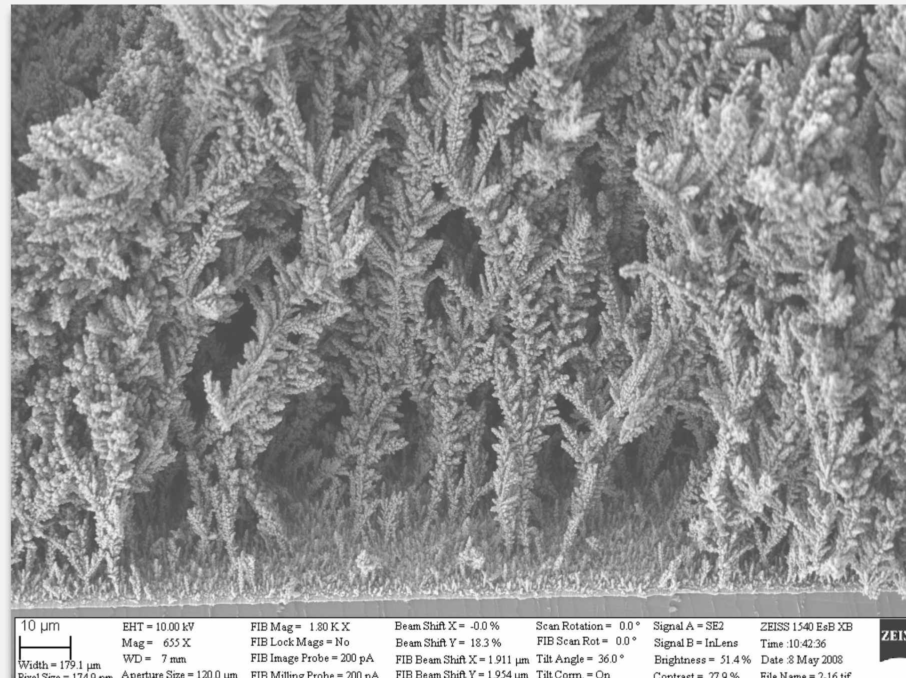
50 nm grain sizes of anode alloy with $Cu_6Sn_5(Fe)$ structure

Structural Analysis
3D Cu Plated on Cu Foil

TOP VIEW



CROSS-SECTIONAL VIEW



100 µm

10 µm

3D Cu porous structure showing micro, meso and nano porosity

3D Cu Anode Development Roadmap

Capacity, mAh/g

1000

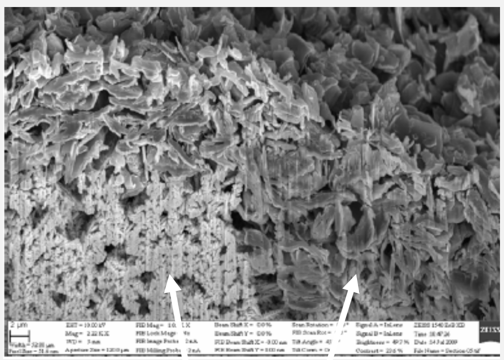
750

500

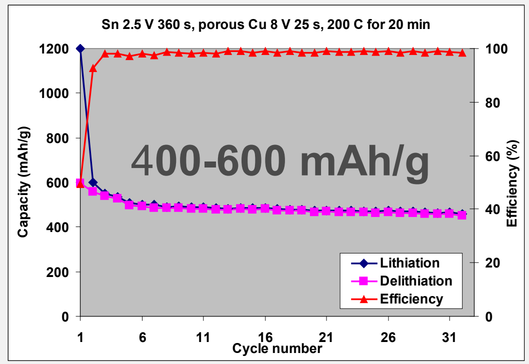
250

Goal: to Develop Next Generation 3D Anode

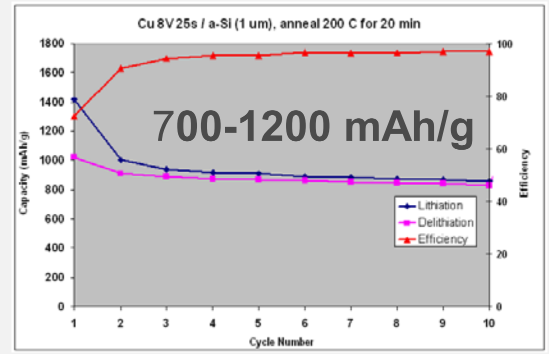
- Capacity
- Current loading
- Cycling lifetime



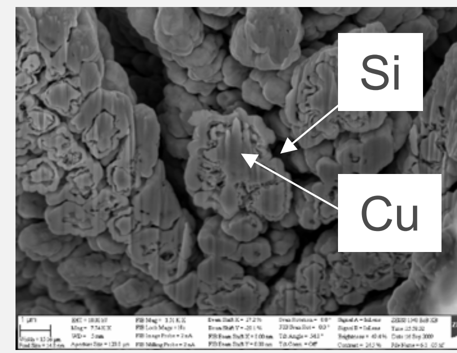
3D Cu + Graphite



3D CuSnFe



3D CuSnFe + Si



3D electrode concept

← Current Technology

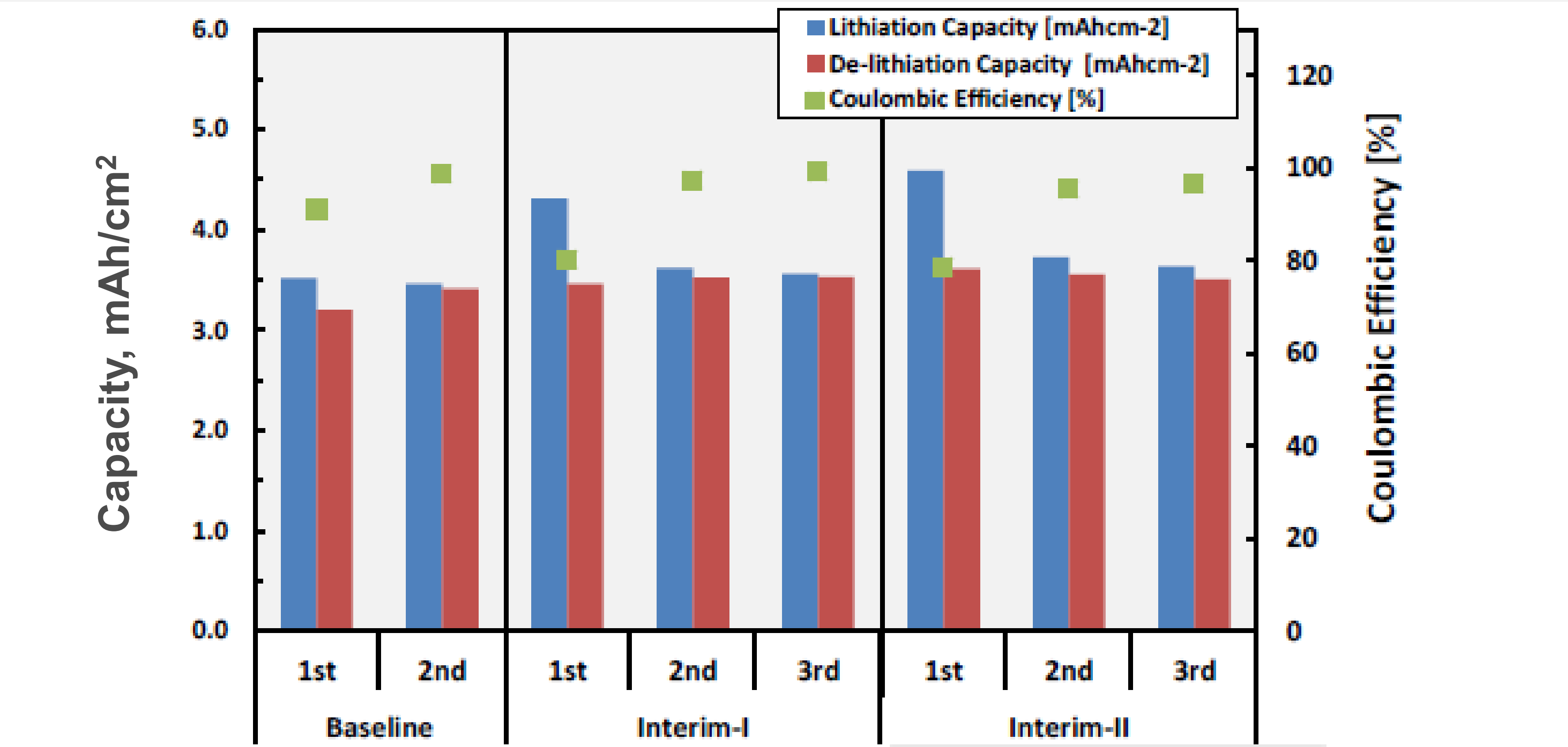
Reduced Anode Cost ($/m^2) and ($/Wh) at Higher Performance

Collaboration:

Navitas (former A123 (cell development)), FMC (pre-lithiation), LBNL(conductive binder)
Nissan-TCNA (testing), ORNL (characterization)

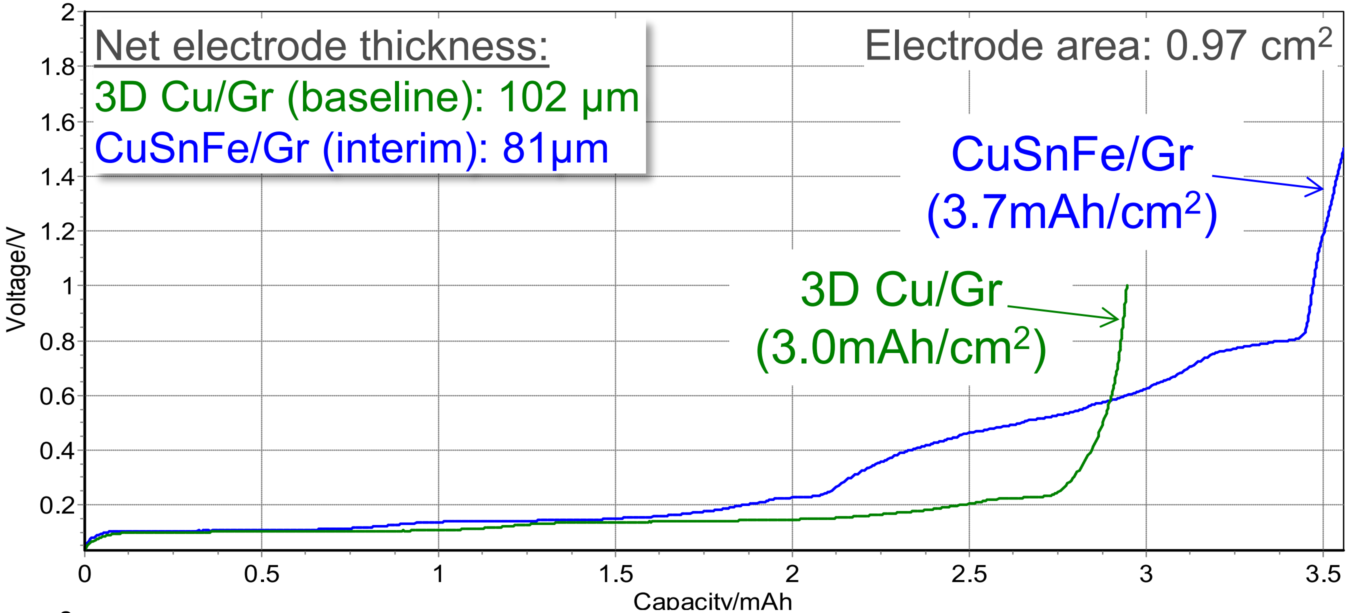
Results
Interim Cell Test

HALF-CELLS: BASELINE 3D Cu/GRAPHITE ANODE and
INTERIM I and II 3D CuSnFe/GRAPHITE ANODES

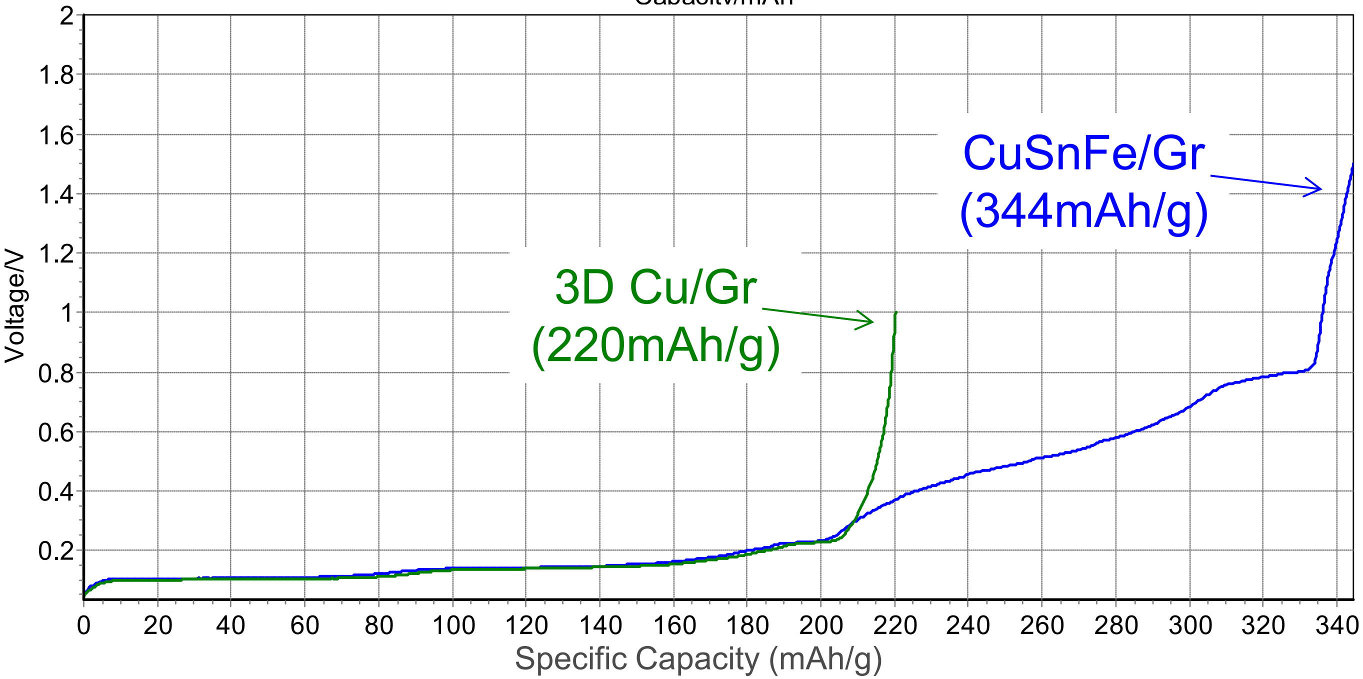


3DCuSnFe/Graphite material – same or higher capacity with 30% thickness reduction

Half Cell Comparison (Interim vs. Baseline)



Specific capacity normalized by ***total net weight of electrode*** including graphite, 3D Cu, binder, and other additives.

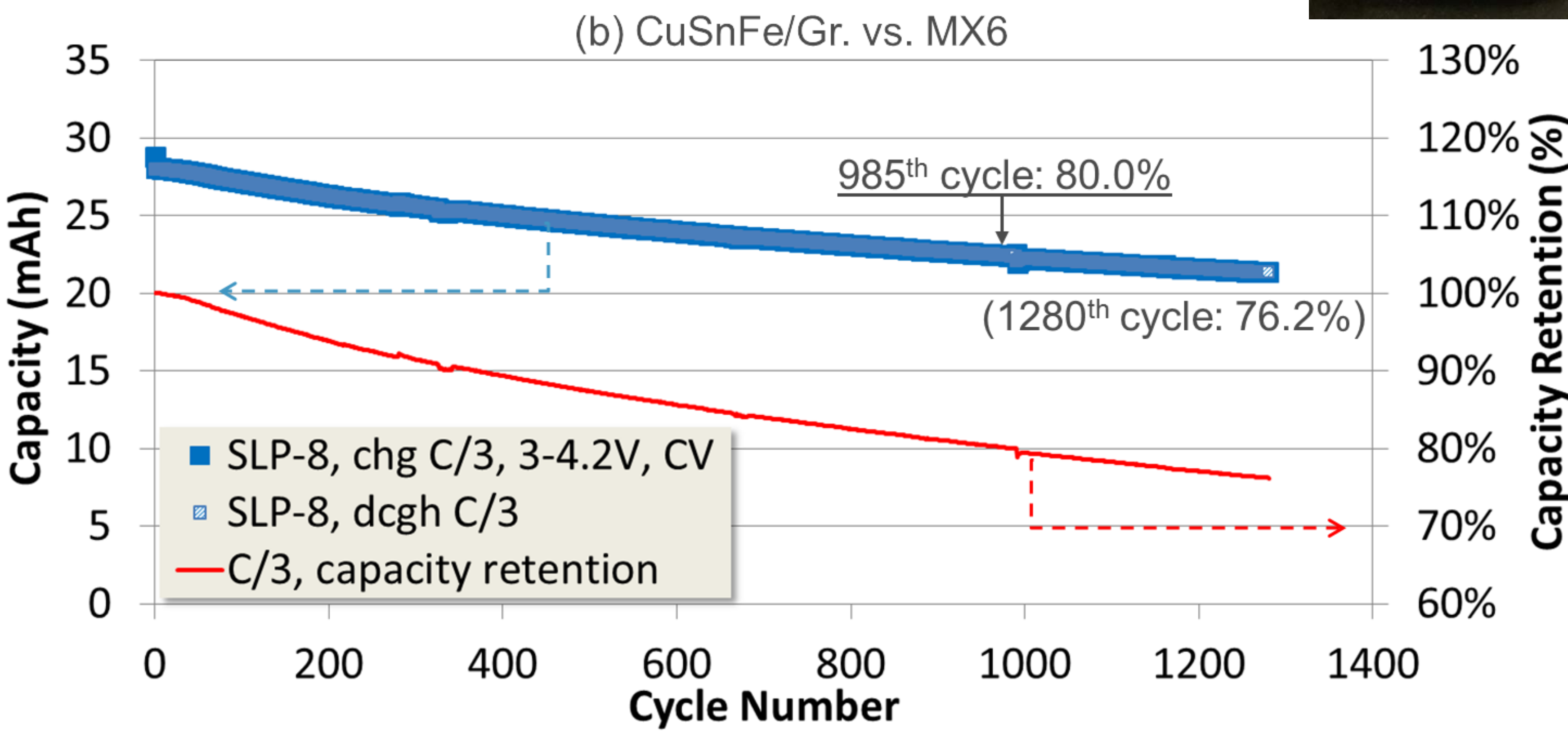


35% increase in specific capacity

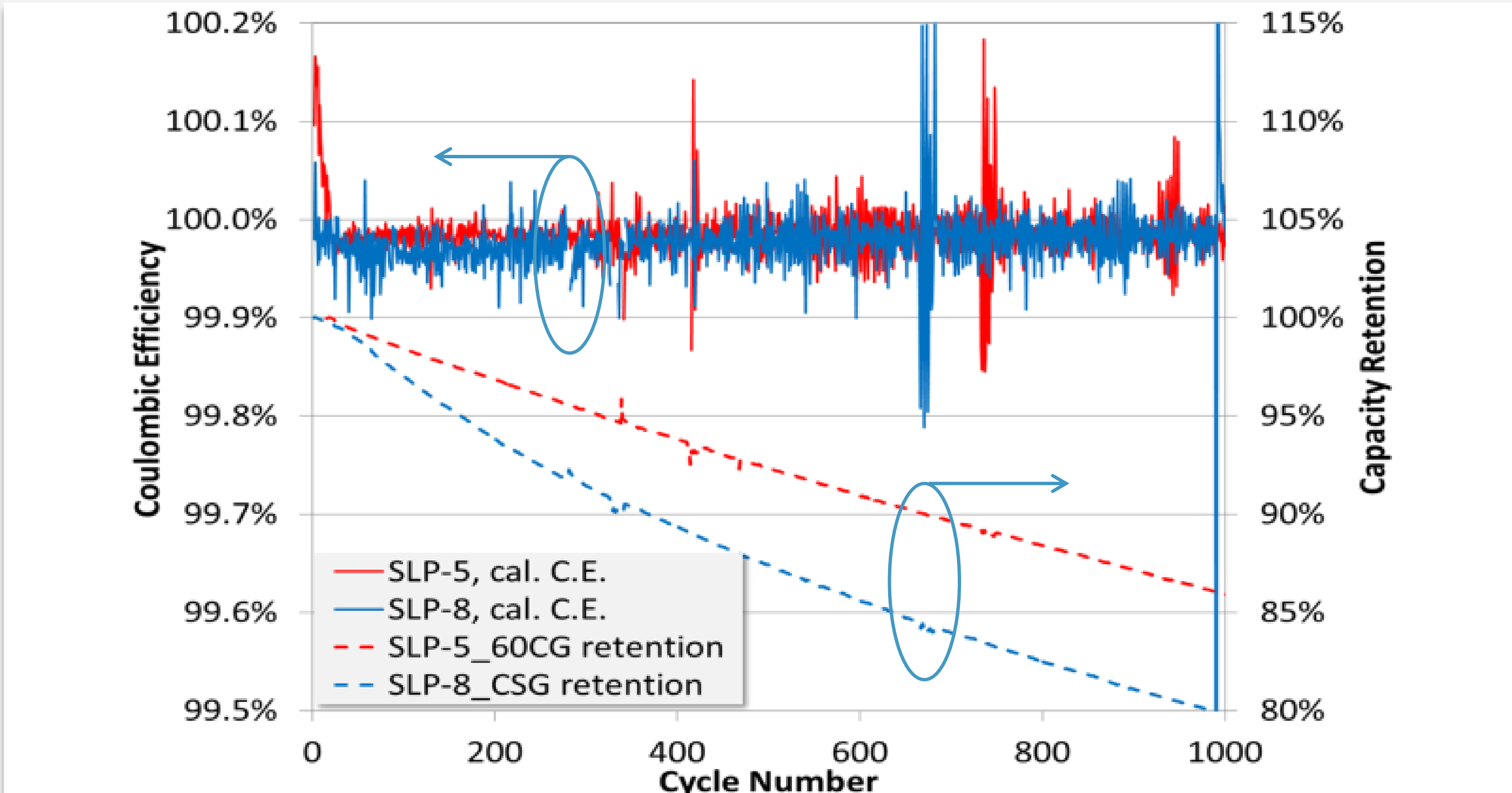
Results

Interim Cell Cycling Test

SINGLE LAYER POUCH CELL SLP-8 WITH
3D CuSnFe/GRAPHITE ANODE AND NMC CATHODE

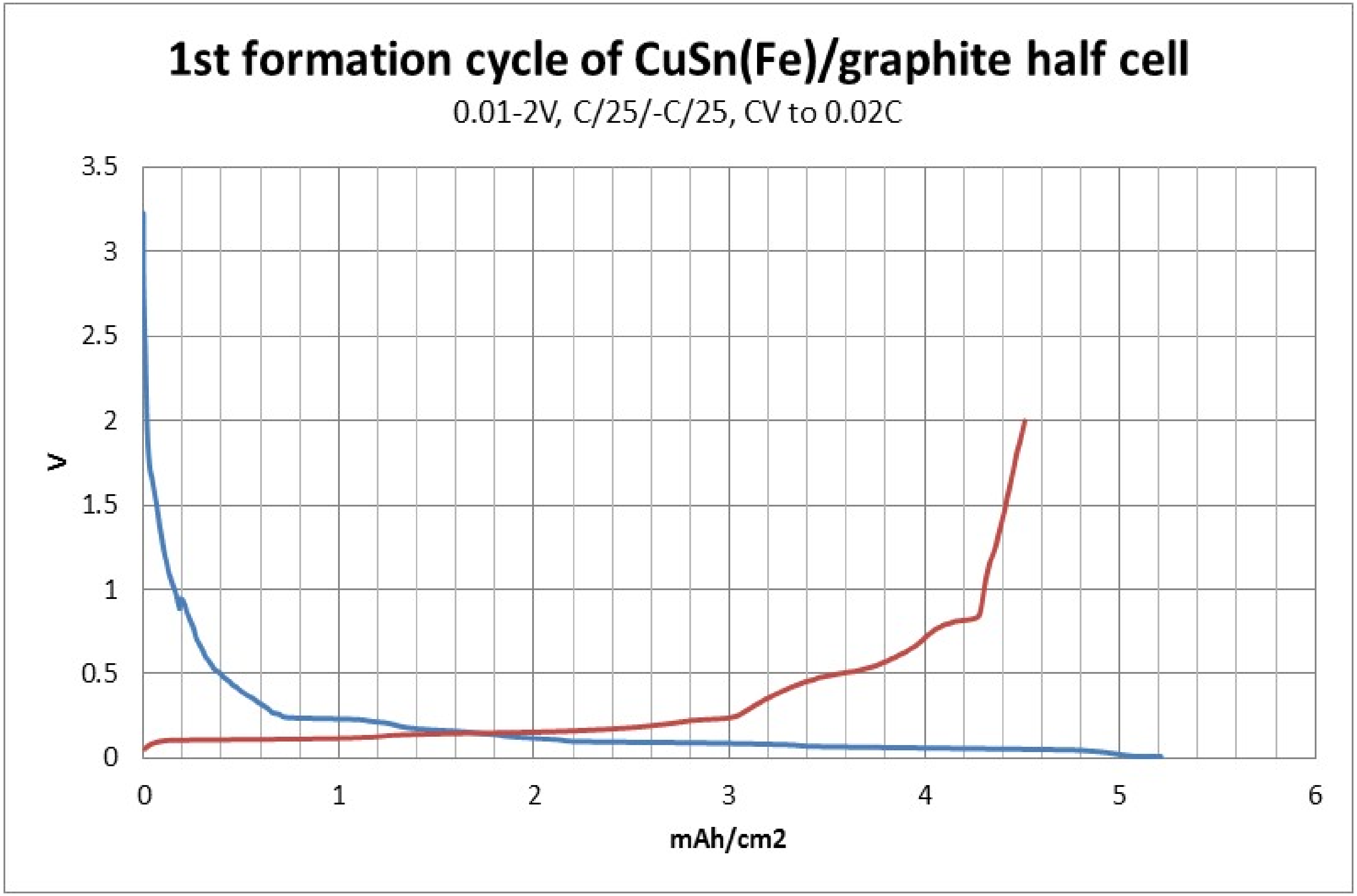


Coulombic Efficiency & Capacity Retention



>99.9% Coulombic Efficiency demonstrated

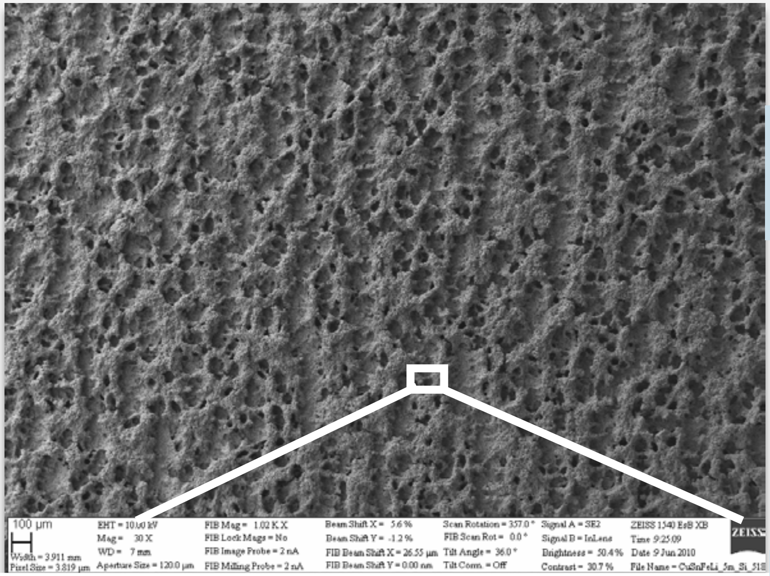
High Current Loading Anode Development



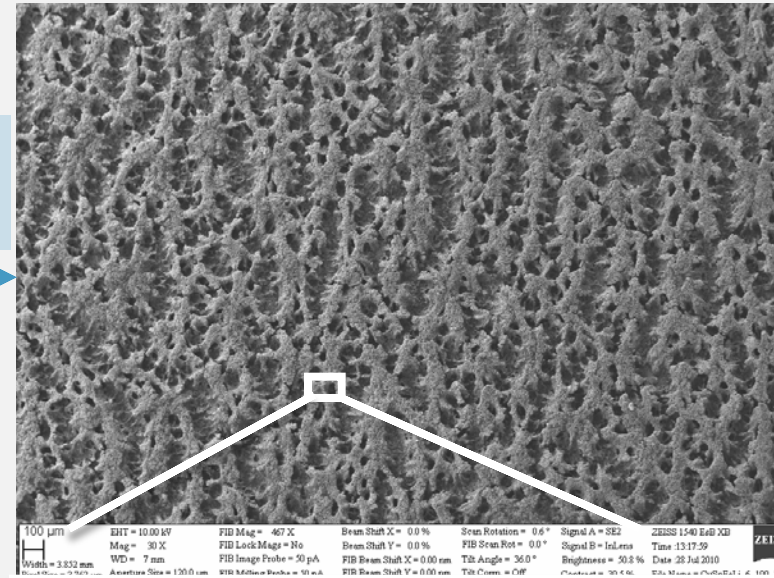
3D CuSnFe/Si Anode for High Loading Cell

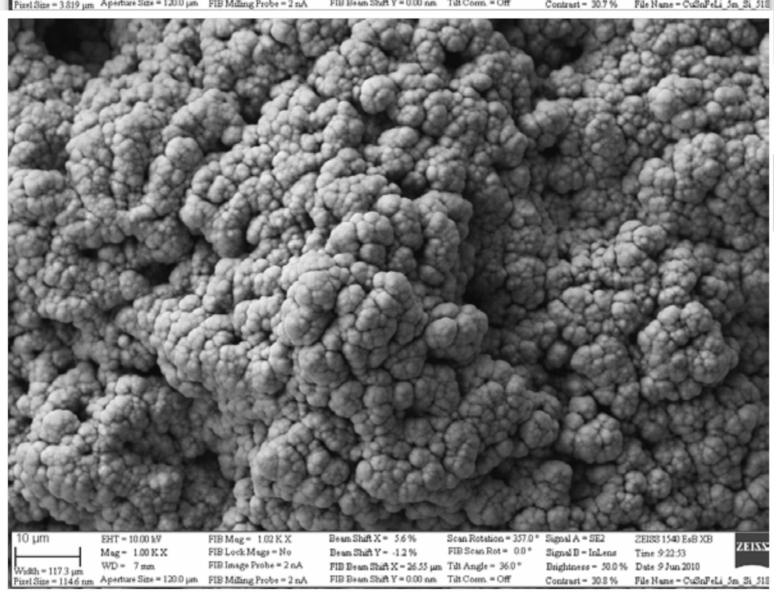
MICRO-METER GRAINS

NANO-METER GRAINS



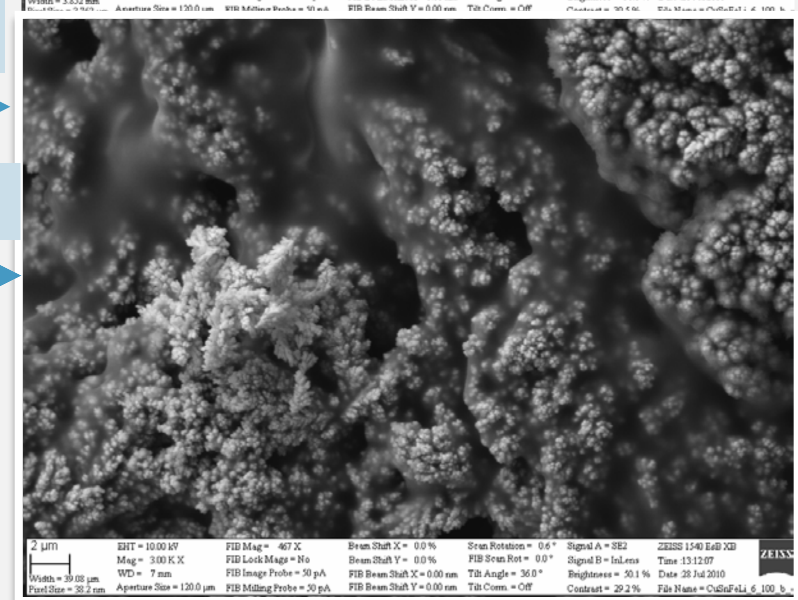
Porosity
Thickness



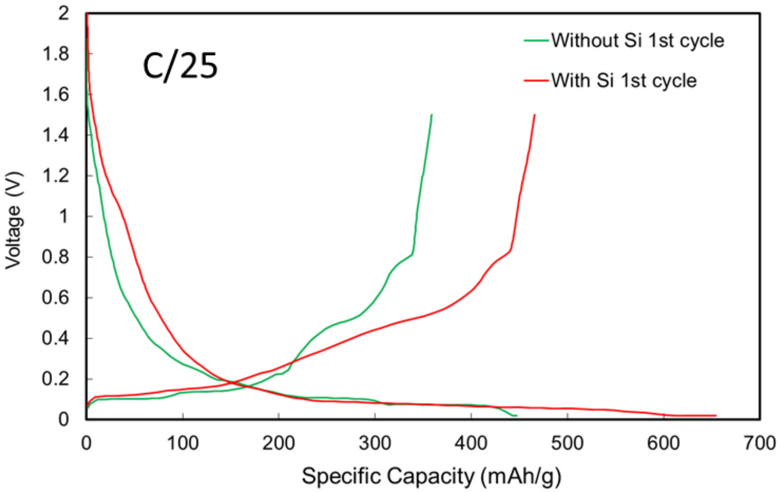


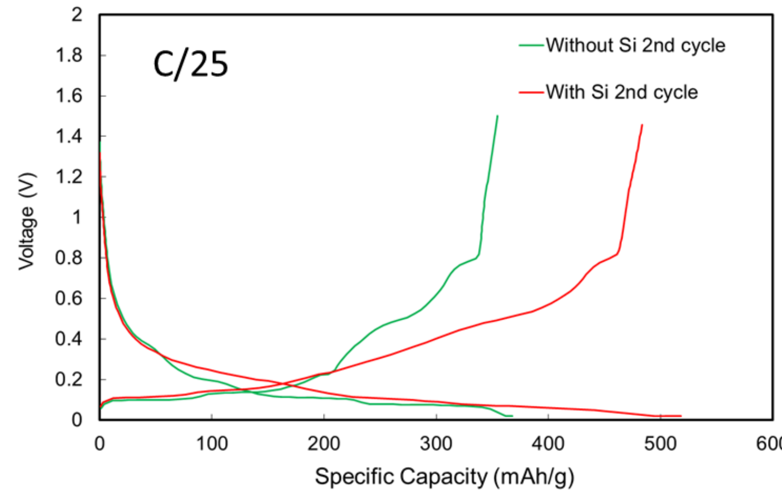
Binder

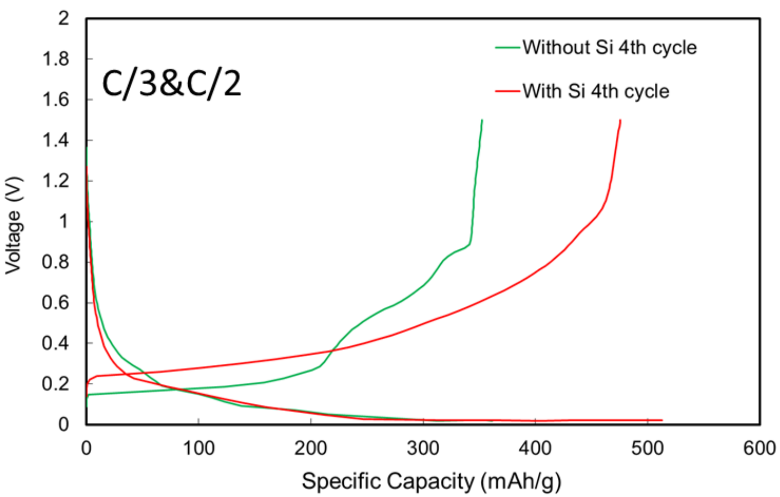
Nano-size

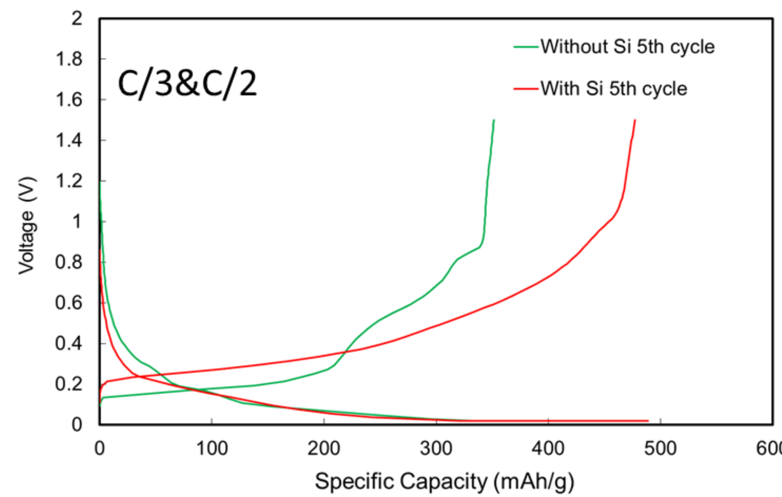


Half Cell Comparison (Final vs. Interim)









30% increase in specific capacity with added Si

Completed Work

TASK 3: BASELINE CELL OPTIMIZATION AND DELIVERABLE

- Demonstrated baseline cell process with 3D Cu/Graphite
- Optimized 3 mAh/cm^2 cell assembly and formation
- Completed capacity retention comparative analysis at 2C and 3C
- Developed thick graphite without cracking for > 3.0 mAh/cm^2 cell
- Completed capacity retention analysis with increased thickness at 2C and 3C

Deliverable 1: Submitted 18 prismatic cells for DOE independent testing

TASK 4: INTERIM CELL DEVELOPMENT

- Optimized high loading CuSnFe/Graphite electrode
- Completed cycling test in full cell assembly

- Next step: During this task the interim cell will be built and sent for characterization and analysis at LBNL and ORNL. Grain size, porosity and other parameters will be characterized for the interim cell deliverable. Applied, Navitas (former A123 Systems) and Nissan TCNA will perform work on extending loading of the anode which will be demonstrated in battery unit.

Project Summary

CONCLUSIONS AND FUTURE DIRECTIONS

- Assembling and testing full prismatic cells with 3D current collectors resulted in Coulombic efficiency over 99.96% at cycles 1000-1400. Projection from the data is that baseline cell with 3DCu/Graphite anode is capable of >1400 cycles at capacity retention of 80% at C/3 rate, and that the interim cell with 3DCuSnFe/Graphite anode is capable of 985 cycles at the same conditions.
- Development of 3DCuSnFe nano-structure alloy anode resulted in half-cell and full cell electrode thickness reduction. Coulombic efficiency (CE) was improved by grain size reduction, pre-lithiation, and mitigation with combining alloy with Graphite.
- Equipment design concept and laboratory scale chamber prototype were developed. Plating module concept incorporated capability to form 3D structure on both sides of the Cu foil. The individual module designs as well as module integration concepts will be fine-tuned. This will allow Applied Materials and project partners to produce the interim and later final sets of cell deliverables for the program. These cells will incorporate the most optimal alloy anode composition.
- Applied Materials and project partners would like to continue development of the alloy anode to further improve the cycling performance. This development allows the benefits of the 3D CuSnFe alloy to be utilized in a higher energy density system.

Acknowledgements

PARTNERS FOR EVALUATION AND TECHNOLOGY VALIDATION

1	Federal Laboratory	**Lawrence Berkeley National Laboratory / Dr. G. Liu**: *Matching anode-cathode for cell balancing, conductive binder and electrolyte additive evaluation*
2	Federal Laboratory	**Oak Ridge National Laboratory / Dr. J. Nanda**: *Materials characterization and degradation analysis using advanced spectroscopic techniques (micro-Raman mapping, X-ray characterization, etc.)*
3	Industry	**FMC Lithium Division / Dr. M. Yakovleva**: *Stabilized Lithium metal powders and coating on anode structures for pre-lithiation*
4	Industry	**Navitas / Dr. P. Hagans**: *Evaluation of Applied Materials electrodes using testing equipment for half coin cell, full coin cell, and full scale 63450 prismatic cell.*
5	Industry	**Nissan Technical Center N. America / Dr. K. Oshihara:** *Cell performance measurements and final cell validation to USABC requirements.*

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Technical Back-Up Slides

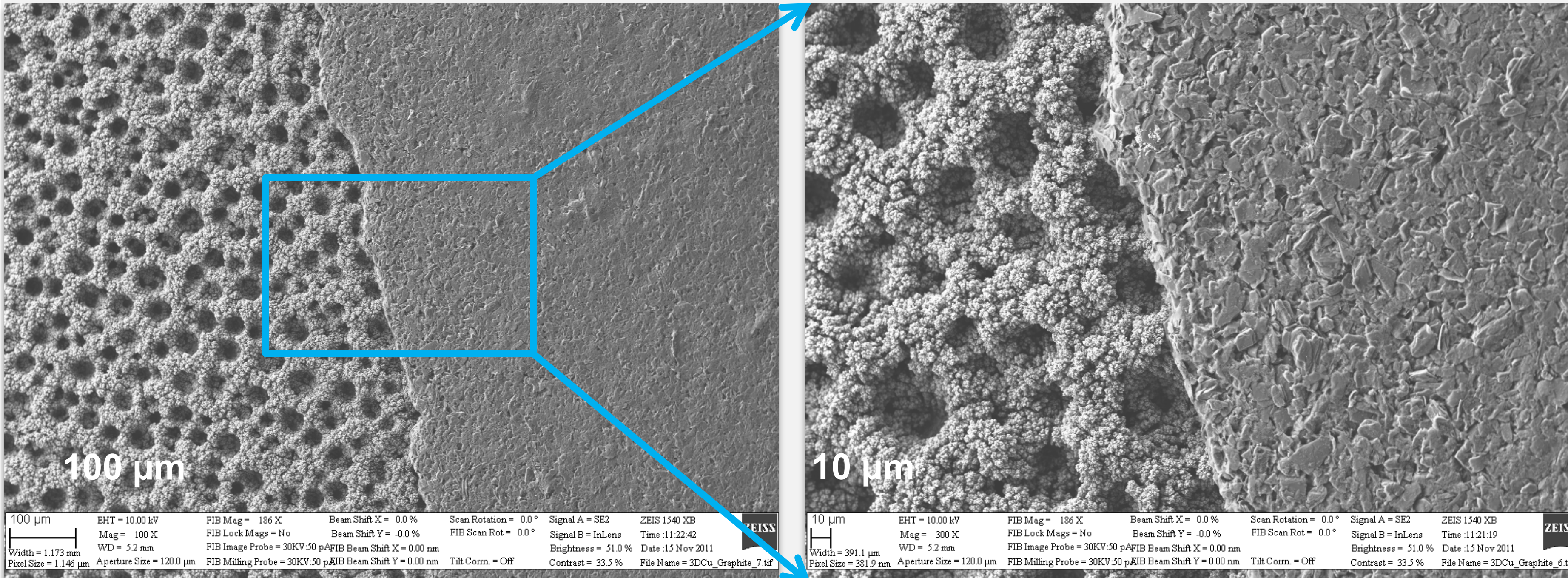
Water-Based Process

For Graphite Coating on 3D Cu

SEM LOWER MAGNIFICATION

SEM HIGHER MAGNIFICATION

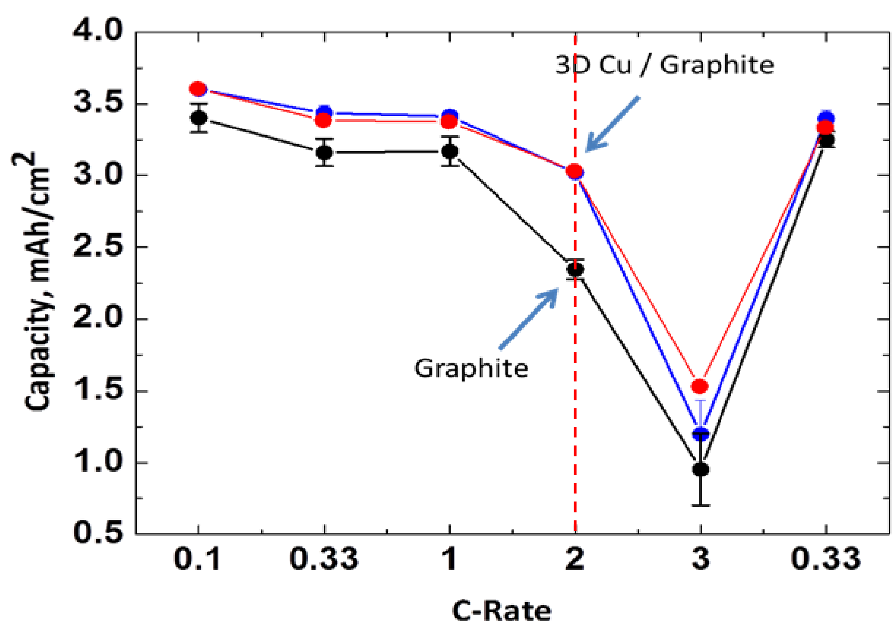
- 3D Cu
- Graphite
- 3D Cu
- Graphite



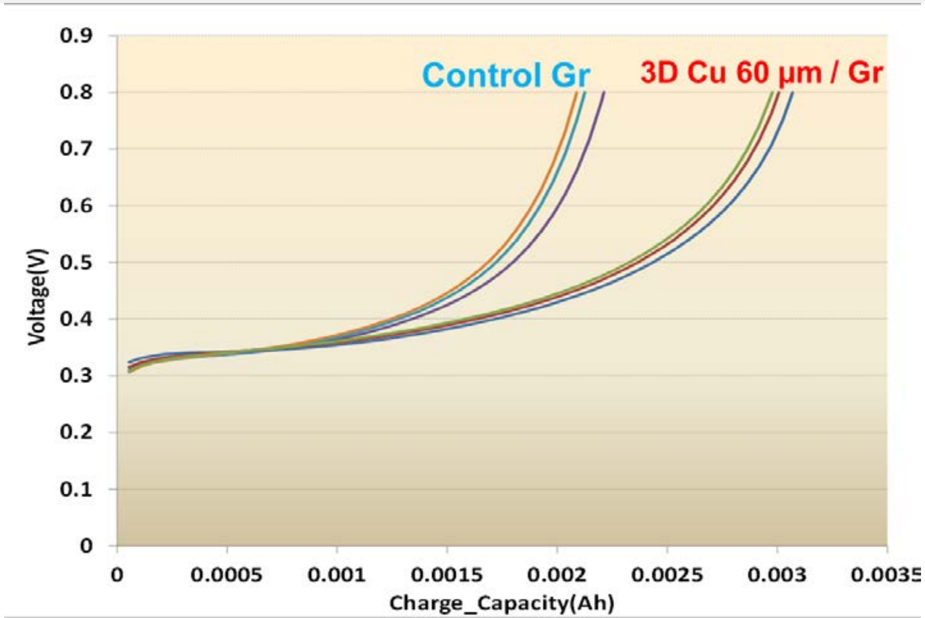
Thick graphite coating with good adhesion and no cracking

C-Rate Advantages

3D Cu/Graphite in Half Cell Tests at >3 mAh/cm² Loadings



Charge capacity of control graphite and 3D Cu 60 µm / Graphite samples at different C-rates



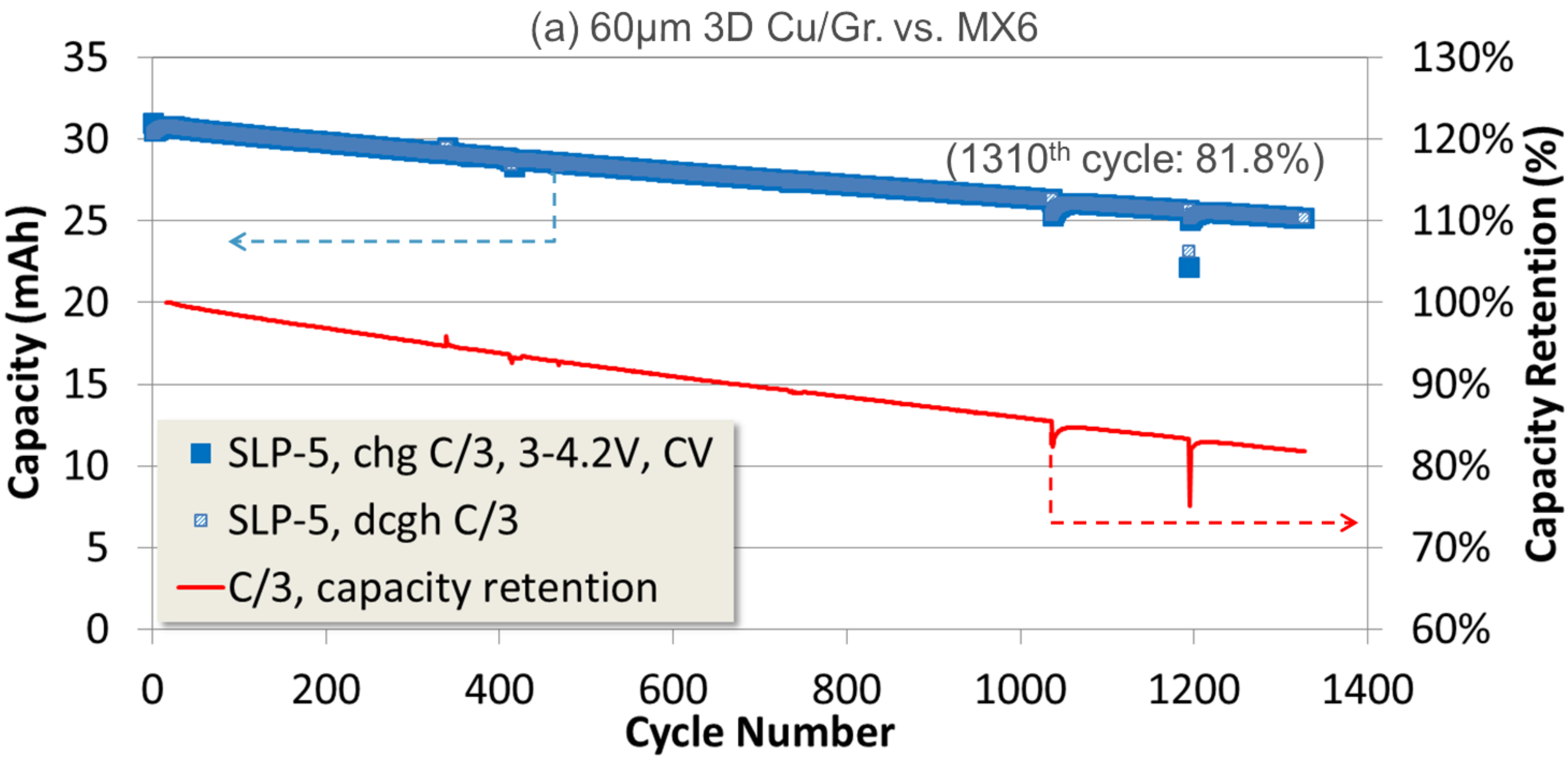
Charge capacity of control graphite and 3D Cu 60 µm / Graphite samples at 2C rate (half cell)

20-24% increase in capacity retention

Results

Baseline Cell Cycling Test

SINGLE LAYER POUCH CELL SLP-5 WITH
60µm 3D Cu/GRAPHITE ANODE AND NMC CATHODE



3D Cu shows good cycle life in full cells

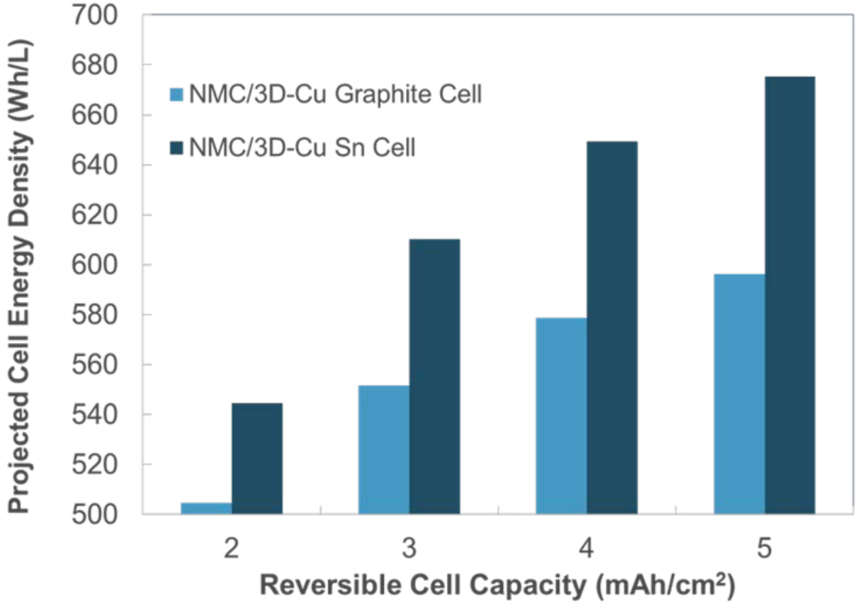
Transition from Baseline Electrode to Interim Alloy Electrodes

Parameters	Baseline	Interim-I	Interim-II
Electrode	3DCu/graphite	CuSn(Fe)/Graphite	CuSn(Fe)/Graphite
Thickness (μm)	109	77	78
Electrode area (cm^2)	4.5 x 11	5x5	5x5
Estimated loading (mAh/cm^2)	3.0	3.0	3.0

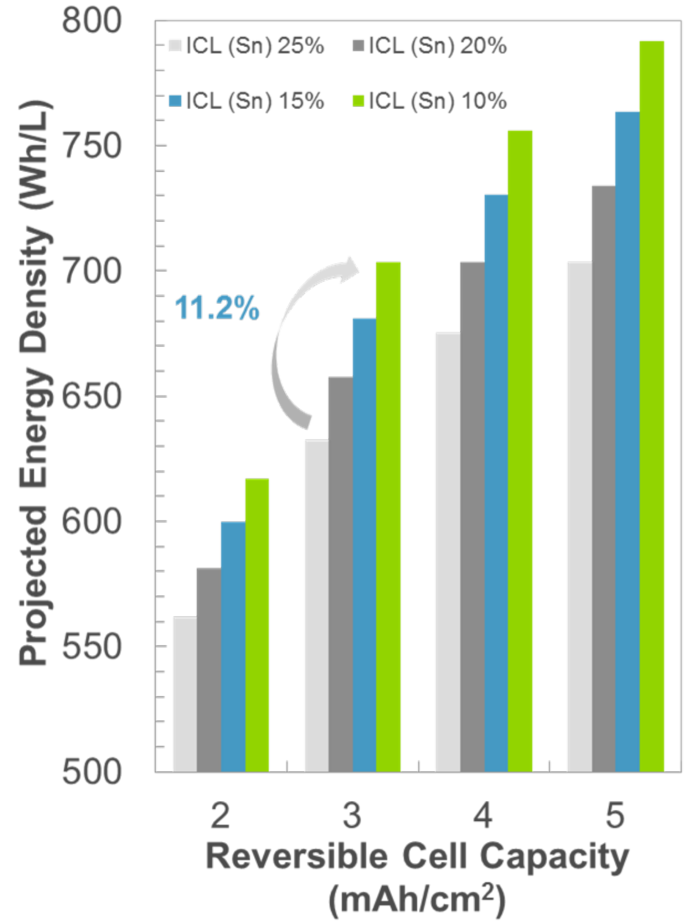
3DCuSnFe/Graphite material with 30% thickness reduction

Modeling Results

Cell Level Design for Baseline and Interim Cells



Project Target >500 Wh/L



Energy density up to 750 Wh/L by reducing Irreversible Capacity Loss

Acknowledgment

“This material is based upon work supported by the Department of Energy under Award Number DE-EE0005455.”

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